Theoretical calculations on adsorption of Sulphur compounds in TS-1 Zeolite

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Abstract

A detailed study on the reaction mechanism of sulphur compounds adsorbed on Ti-Silicalite-1 (TS-1 zeolite) Catalysts has been carried out using DFT method at the B3LYP-D3/6-31G(d, p) level. Through structural design and optimization, the optimum hydrolysis position and adsorption of methyl mercaptan, dimethyl sulfide and thiophene on Ti10@5T TS-1 zeolite were analyzed. The adsorption of three sulfur compounds with hydrolytic Ti10@5T TS-1 zeolite was the most stable. The finding is important to support related experimental research.

Keywords

TS-1; adsorption; Sulphur compounds.

1. Introduction

With the development of TS-1 zeolite with Four coordination Ti (IV) MFI construction by Taramasso at 1983[1], the catalysis research reached a new level from acid catalysis to oxidation catalysis. TS-1 zeolite is a kind of selective oxidation catalysts on organic oxidation reactions with H_2O_2. And the TS-1 zeolite has been applied to hydroxylation of aromatic groups [2], oxidation of chain hydrocarbons [3], oximation of cyclohexanone [4], etc.

Sulfide from gasoline combustion is one of the major air pollutants [5]. With the attention of people to environmental problems, many studies focus on deep desulfurization of fuels [6-9]. Du et al [10] have studied the effects of drying temperature, water content and grinding procedure on the morphology of TS-1, which is a very promising catalyst for deep oxidation desulfurization.

Li et al [11] have applied the density function theory to investigate the structure of the framework titanium species in the Ti-YNU-1 zeolite, and discussed the barrier of 1-hexene epoxidation over different Ti active centers. Zhou et al. [12]reported that the Ti^{4+} species in form of $Ti(OSi)_4$ prefers to locate at the T1 and T3 sites, when the Ti^{4+} species were substituted at different T sites.

Yuan et al [13] have studied the location of Si vacancies and [$Ti (OSi)_4$] and [$Ti(OSi)_3OH$] sites in the MFI framework with ab initio method, and got the conclusion that the former four energetically favorable sites for Si vacancies areT6, T12, T4, and T8 and for Ti centers of [$Ti(OSi)_4$] are T10, T4, T8 and T11, being partially the same sites.

At present, the desulfurization effect and influencing factors of TS-1 zeolite have been well studied [10, 14, 15], but the adsorption between hydrolytic type (defect type) and non-hydrolytic type (perfect configuration) of TS-1 zeolite and sulfur-containing compounds has not been studied. As we known, the active centers of TS-1 are Ti sites in the crystallite, which bonded in the TS-1 lattice.[16, 17] In this paper, the model TS-1 Ti10@5T was used to study the different adsorption configurations of the perfect and defective molecular sieves on sulfur-containing compounds by using the quantitative calculation method, and the interaction among different adsorption configurations was also discussed. The results can provide theoretical support for related experimental research.

2. The Construction of the Model and calculation method

2.1 The Construction of the Model

Based on Gaussian software, in order to obtain more accurate results, the titanium silica molecular sieve will adopt the 5T model, select T10 as the Ti substitution, remove the adjacent Si, saturation the suspended bond with hydrogen atom, and optimize the bond length and the bond angle of the hydrogen bond at the same time. The outermost layer of the atom is saturated with a hydrogen atom in the original direction, that is, in the direction of bonding with the next oxygen atom. The Si and H bond lengths of 0.146 nm were set to keep the position of hydrogen atoms unchanged in order to reflect the skeleton structure of molecular sieve and the other atoms were freely optimized. Here hydrogen atoms rather than OH are chosen to saturate the suspended bonds in order to avoid unnecessary hydrogen bonds in the optimization process.

2.2 Calculation method

Using the B3LYP-D3 method of density functional theory (DFT-D)[18, 19], the structure of reactants, intermediates, transition states and products in the reaction system was optimized at 6-31g (d, p) basis group level. In structural optimization, the coordinates of the outermost two layers of atoms in the cluster model are fixed (represented by a linear model in this paper) to ensure the rigidity of the molecular sieve, and the rest of the skeleton atoms are relaxed and optimized (represented by the spherical stick model in the graph). The correctness of the transition state is confirmed by vibration analysis. In order to obtain more accurate reaction energy barrier, the single point energy is calculated at B3LYP-D3/def2-TZVP level. All the above calculations were completed by gaussian 16A.03 program [20].

3. Result and Discussion

3.1 Configuration of Titanium Oxide Active Intermediate

In TS-1molecule, $Ti(OSi)_4$ and $Ti(OSi)_3OH$ have tetrahedron symmetry. In $Ti(OSi)_4$, the average bond length of Ti-O bond is 1.765 Å, the average bond length of O-Si bond is 1.642 Å, the average bond angle of Ti-O-Si is 136.06°, and the average bond angle of O-Ti-O is 109.47°. The local structure of the $Ti(OSi)_4$ unit is shown in Fig. 1. There are four different hydrolysis sites for $Ti(OSi)_4$ in the formation of $Ti(OSi)_3OH$, because of the Si1, Si9, Si10 and Si11 sites connected to Ti in T10 TS-1 zeolite. The geometric configuration and related data are shown in Fig. 2 and Table 1

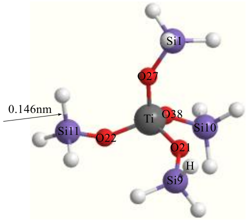
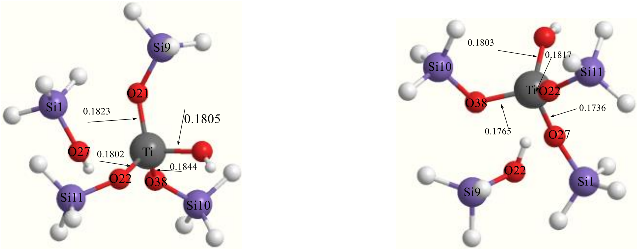
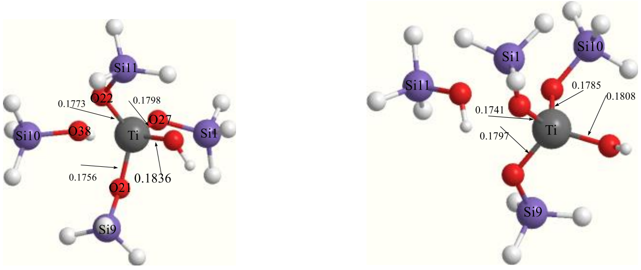


Figure 1 Ti10@5T titanium silicon molecular sieve structure diagram



a. hydrolysis on Si1 of Ti10@5T b. hydrolysis on Si9 of Ti10@5T



c. hydrolysis on Si10 of Ti10@5T d. hydrolysis on Si11 of Ti10@5T

Figure 2 geometric structures of titanium silicon molecular sieves with different hydrolysis positions

Table 1 geometric data of different hydrolysate titanium silicon molecular sieves

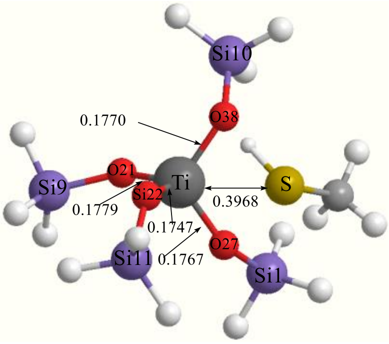
Si	Ti-O(nm)	O-Si(nm)	Ti-O-Si(°)	Ti-O(nm) (Hydrolysis site)	O-Ti-O(°)
Si1	0.1823	0.1663	136.6	0.1805	108.8
Si9	0.1773	0.1675	140.2	0.1803	106.1
Si10	0.1776	0.1641	125.4	0.1836	108.5
Si11	0.1774	0.1643	128.7	0.1808	109.3

Considering the spatial structure, the sulfur-containing molecules in the un-hydrolyzed TS-1 zeolite will approach the tetrahedron Ti center along the channel. Considering the space environment, the sulfur-containing compounds in hydrolyzed TS-1 zeolite will be close to the Ti center or the hydrolysate hydroxyl groups connected with Ti. The geometrical structure of the adsorption of sulfur-containing compounds and sulfur-containing compounds from the sites and centers of hydrolytic TS-1 zeolite has been obtained by optimization calculation. The geometric parameters and binding energy of the optimized system are summarized in Table 2. For the sake of clarity, the local structure of the adsorption unit is shown in figure 3.

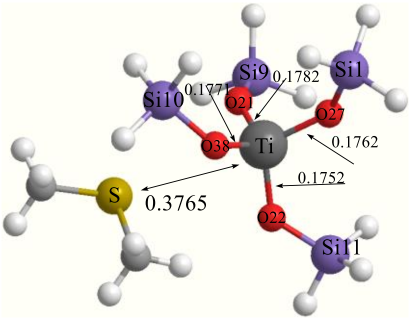
Table.2 geometric structure of hydrolytic and non-hydrolytic titanium silicon after sulfur compounds adsorption

Sulfide / molecular sieve	Ti-O (nm)	O-Si (nm)	O-Ti-O(°)	O-T-O(°) Before adsorption	Hydrolysis siteTi-O(nm)	Distance between S and Ti（nm）
methanethiol/Ti(OSi)4	0.1766	0.1646	110.3	109.5		0.3968
methyl sulfide/Ti(OSi)4	0.1767	0.1644	109.2	110.4		0.3765
thiophene/Ti(OSi)4	0.1766	0.1644	108.3	109.4		0.3662
methanethiol/Ti(OSi)3OH	0.1785	0.1636	98.9	107.3	0.1849	0.2975
methyl sulfide/Ti(OSi)3OH	0.1779	0.1643	108.6	107.3	0.1791	0.4138
thiophene/Ti(OSi)3OH	0.1774	0.1644	104.3	104.9	0.1816	0.3570
methanethiol/Ti(OSi)3OH	0.1796	0.1646	111.1	110.6	0.1803	0.4404
methyl sulfide/Ti(OSi)3OH	0.1793	0.1635	97.5	107.3	0.1853	0.2746
thiophene/Ti(OSi)3OH	0.1777	0.1641	106.3	106.6	0.1796	0.3606

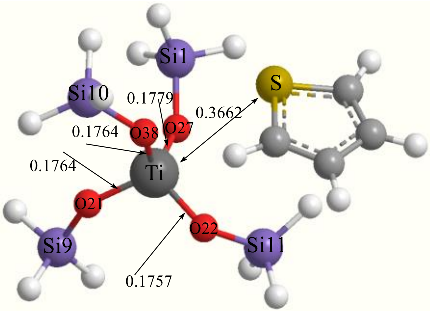
Note: underlined atoms are close to ligands



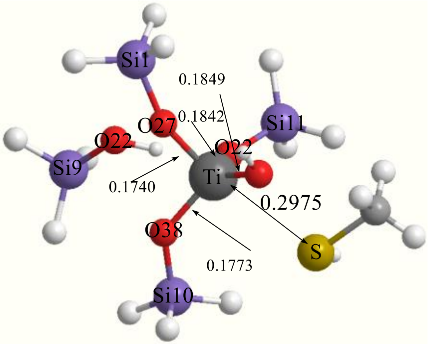
a. methanethiol adsorb on Ti10@5T



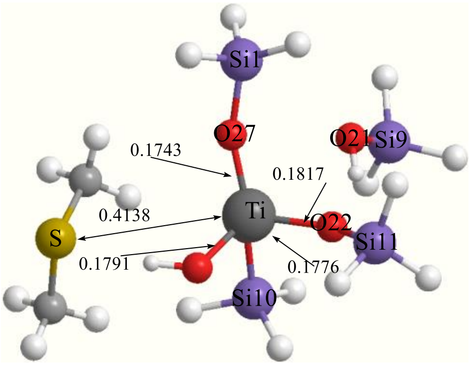
b. methyl sulfide adsorb on Ti10@5T



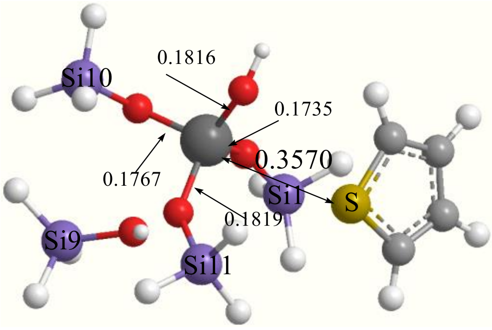
c. thiophene methanethiol adsorb on Ti10@5T



d. methanethiol adsorb on Ti10@5T hydrolysis site

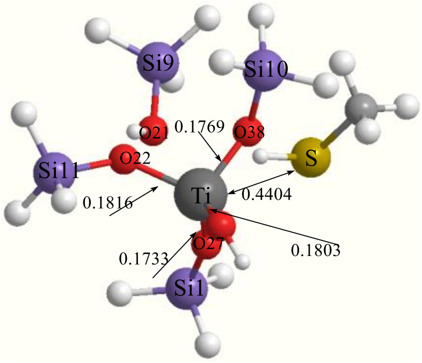


e. methyl sulfide adsorb on Ti10@5T hydrolysis site

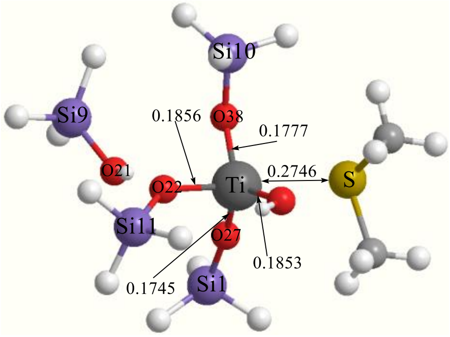


f. thiophene adsorb on Ti10@5T

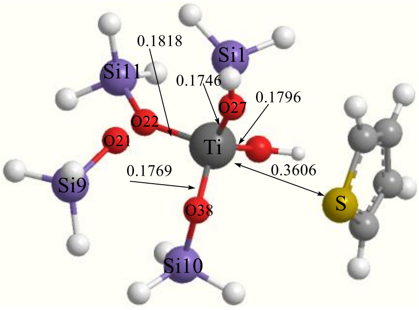
hydrolysis site



g.methanethiol adsorb on hydrolytic
Ti10@5T central titanium position



h. methyl sulfide adsorb on hydrolytic
Ti10@5T central titanium position



i. thiophene adsorb on hydrolytic Ti10@5T central titanium position

Fig. 3 structure of sulfur compounds adsorb on TS-1 zeolite

It can be seen from Table 2 that ligand adsorption leads to the transition of molecular sieve from tetrahedron structure to triangular biconical structure, and the induction of sulfur-containing compounds increases the average bond length of Ti-O bond of hydrolyzed TS-1 zeolite by -0.0002-0.0017nm. The average bond length of un-hydrolyzed Ti-O bond increases by 0.0001-0.0002nm. The average bond length of Si-O bond increases by -0.0006-0.0005nm, The Si-O bond length of the un-hydrolyzed TS-1 zeolite increased by 0.0002-0.0004nm, meanwhile the average bond angle of O-Ti-O changed between -9.85-1.3°. As can be seen from the above data that adsorption has certain influence on molecular sieve structure.

3.2 Energy Analysis

The binding energies of all Ti-Si molecular sieves adsorbing sulfur-containing compounds have been showed in Table 3. The binding energy of sulfur compounds adsorbed to the center of Ti of hydrolytic TS-1 zeolite was significantly higher than that of sulfur-containing compounds adsorbing on the hydrolytic sites of non-hydrolytic TS-1 zeolite and hydrolytic TS-1 zeolite. Table 4 showed that the binding energy of un-hydrolyzed TS-1 zeolite adsorbed on sulfur-containing compounds was higher than that on hydrolytic hydroxyl groups of hydrolytic TS-1 zeolite, which indicated that the sulfur-containing compounds were more inclined to adsorb on the central Ti atoms. The adsorption of sulfur-containing compounds with hydrolyzed Ti10@5T is the most stable.

Table 3 The optimum hydrolytic position, hydrolysis energy and adsorption energy of sulfur compounds

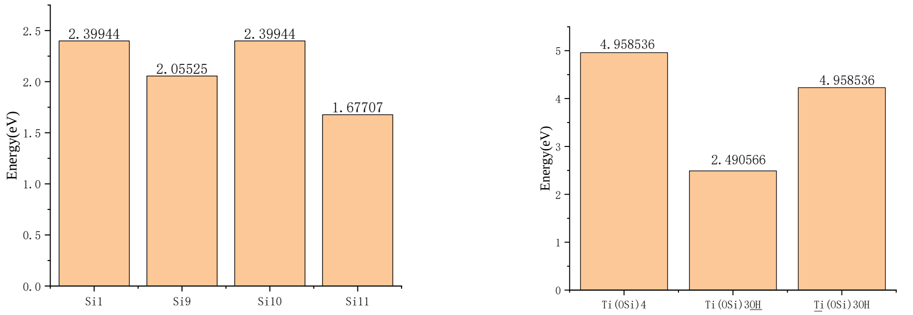
Sulfide / molecular sieve	ΔE (KJ/mol)
Hydrolysis of Si1	97.28
Hydrolysis of Si9	-29.70
Hydrolysis of Si10	49.49
Hydrolysis of Si11	1.28

Table 4 Adsorption energy of sulphur containing compounds

Sulfide / molecular sieve	ΔE (KJ/mol)
methanethiol/Ti(OSi)_4	-31.42
methyl sulfide/Ti(OSi)_4	-34.35
thiophene/Ti(OSi)_4	-43.54
methanethiol/$\text{Ti(OSi)}_3\underline{\text{OH}}$	-14.98
methyl sulfide/$\text{Ti(OSi)}_3\underline{\text{OH}}$	-45.7
thiophene/$\text{Ti(OSi)}_3\underline{\text{OH}}$	-35.97
methanethiol/$\underline{\text{Ti}}\text{(OSi)}_3\text{OH}$	-35.17
methyl sulfide/$\underline{\text{Ti}}\text{(OSi)}_3\text{OH}$	-49.92
thiophene/$\underline{\text{Ti}}\text{(OSi)}_3\text{OH}$	-46.32

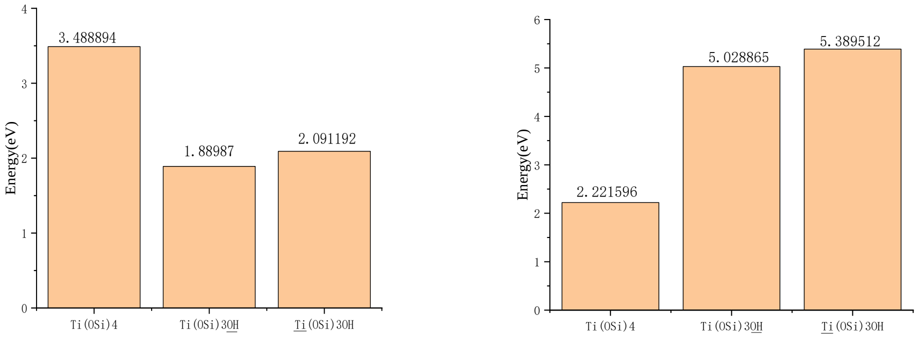
3.3 Frontier Molecular Orbit（FMO）Analysis

Frontier Molecular Orbital (FMO) analysis has been used to better understand the energy of TS-1 zeolite before and after hydrolysis at T10 site and to adsorb sulfur-containing compounds. According to FMO theory, the smaller the difference of HOMO-LUMO energy is, the easier chemical reaction takes place. In figure 4, we showed the energy levels of HOMO and LUMO in each reaction and adsorption process. It is shown in the diagram that the HOMO-LUMO energy difference of $Ti(OSi)_4$-thiophene is the minimum when adsorbing the same kinds of sulfur-containing compounds. The HOMO-LUMO energy difference of methyl sulfide absorbed on $Ti(OSi)_3$OH hydrolyzed hydroxyl position is the smallest.



LUMO/HOMO energy difference at hydrolysis sites of Ti10@5T

LUMO/HOMO energy difference of CH4S absorb on different site



LUMO/HOMO energy difference of C2H6S absorb on different site

LUMO/HOMO energy difference of Thiophene absorb on different site

Fig. 4 HOMO and LUMO energy level of sulfur compounds adsorb on TS-1 zeolite

3.4 NPA Charge Analysis

Charge transfer is the driving force of chemical reaction. Using NPA analysis can better describe the charge distribution in compounds. Now more qualitative evidence has been obtained for the above structure analysis. In order to further understand the hydrolysis reaction of TS-1 zeolite (TS-1 Ti10@5T) and the adsorption of hydrolytic TS-1 zeolite and non-hydrolytic TS-1 zeolite with sulfur-containing compounds, we list the NBO charges of Ti10@5T in tables 5 to 6.

Table 5 NPA charge of each atom on the Ti10@5T hydrolysate

Atom	Si1	Si9	Si10	Si11
Si1	1.18	1.22	1.20	1.21
O21	-0.89	-0.80	-1.07	-0.86
O22	-0.90	-0.82	-1.03	-0.89
O27	-0.92	-0.82	-1.08	-0.88
O38	-0.91	-0.83	-1.11	-0.88
O7	-1.09	-1.01	-0.97	-1.06
Si10	1.24	1.20	1.23	1.21
Si9	1.22	1.19	1.27	1.24
Si11	1.23	1.24	1.19	1.18
Ti24	1.31	1.01	1.84	1.25

Table 5 shows that the Ti24 charge can reach 1.76 and C26 charge can reach -0.85 when the hydroxyl group adsorbs methyl sulfide at the hydrolytic Ti10@5T hydrolysis position, the interaction between them is the largest. Methyl sulfide is different from the analysis of adsorption energy. The adsorption of the other two sulfur-containing compounds is the same as that of adsorption energy.

Table 6 NBO charge of non hydrolytic Ti10@5T TS-1 zeolite adsorbed sulfur compounds

Atom	methanethiol/Ti(OSi)4	Atom	methyl sulfide/Ti(OSi)4	Atom	thiophene/Ti(OSi)4
Si1	1.22	Si1	1.21	Si1	1.18
Si2	1.23	Si2	1.23	Si2	1.23
Ti3	1.85	Ti3	1.51	Ti3	1.24
Si4	1.24	Si4	1.24	Si4	1.24
O5	-1.07	O5	-1.09	O5	-1.02
O6	-1.07	O6	-1.05	O6	-1.09
O7	-1.05	O7	-1.02	O7	-1.02
O8	-1.02	O8	-1.02	O8	-1.01
Si9	1.22	Si9	1.21	Si9	1.21
C22	-0.81	S22	0.53	C22	-0.50
S26	-0.08	C23	-0.83	C 23	-0.28
		C27	-0.83	C 24	-0.34
				C 25	-0.52
				S 26	1.10

Table 6 shows that the Ti24 charge can reach 1.87 and C25 charge can reach -0.82 when methionol absorbed on hydrolyzed Ti10@5T center, the interaction between them is the largest. While the Ti24 charge can reach 1.88 and C25 charge can reach -0.46 when thiophene adsorbed.

4. Conclusion

In this work, DFT-D calculations on the hydrolysis configuration of TS-1 and its adsorption with sulphur compounds have been studied. The results of hydrolysis adsorption of TS-1 zeolite at Si9 site showed that the adsorption of titanium between the three kinds of sulfur-containing compounds and the center of hydrolyzed Ti10@5T TS-1 zeolite was the most stable. The results of NPA charge analysis showed that the charge of methyl mercaptan and thiophene adsorbed by titanium in the center of Ti10@5T was the strongest, and the charge of dimethyl sulfide on hydrolysate position of hydrolyzed Ti10@5T was the strongest. Adsorption of Titanium on the Center of hydrolyzed Ti10@5T TS-1 zeolite with adsorption Energy as Standard three sulphur compounds are the most stable.

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